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The Effect of Filler-Polymer Interactions on Cold-Crystallization Kinetics in Crosslinked, Silica Filled PDMS/PDPS Copolymer Melts.

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ABSTRACT

Crystallization in a series of variable crosslink density poly(dimethyl-diphenyl) siloxanes random block copolymers reinforced through a mixture of precipitated and fumed silica fillers has been studied by Differential Scanning Calorimetry (DSC), Dynamic Mechanical Analysis (DMA), and X-ray Diffraction (XRD). The silicone composite studied was composed of 94.6 mol% Dimethoylsiloxane, 5.1 mol% diphenylsiloxane, and 0.3 mol% methyl-vinyl siloxane (which formed crosslinking after a peroxide cure). The polymer was filled with a mixture of 21.6 wt. % fumed silica and 4.0 wt. % precipitated silica previously treated with 6.8 wt. % ethoxy-endblocked siloxane processing aid. The base composite was characterized by a molecular weight between crosslinks in the polymer network of ~24 kDa and an overall molecular weight (including the influence of the silica fillers) between crosslinks of ~11 kDa. Molecular weight between crosslinks and filler-polymer interaction strength were then modified by exposure to γ-irradiation in either air or vacuum. The unirradiated material exhibited crystallization at –80 ºC as measured by DSC with a 16% crystallization as measured by XRD. Isothermal DMA experiments illustrated that crystallization at –85°C occurred over a 1.8 hour period in silica-filled systems and 2.2–2.6 hours in unfilled systems. The onset of crystallization typically occurred after a 30-minute incubation/nucleation period. The crystallization kinetics were dependent on crosslink density. Changes in molecular weight of a factor of two did not, however, change the amount of crystallization. Irradiation in vacuum resulted in faster overall crystallization rates compared to air irradiation for the same crosslink density, likely due to a reduction in the interaction between the polymer chains and the silica filler surface. Modulated differential scanning calorimetry contrasted the crystallization and melting behavior of pure PDMS versus the PDMS/PDPS base copolymer and helped determine which component of the composite was the origin of the crystallization phenomena.

KEYWORDS:

Crystallization, crosslink density, filled siloxane polymers, DSC, isothermal DMA

INTRODUCTION:

The properties of filled-polymer composite systems are governed by the components of the composite including polymer and filler compositions, filler size and morphology, and strength of the interfacial bonding between the polymer and the filler phases.[1-3] Silica filled polydimethylsiloxane (PDMS) based systems, for example, are known to exhibit cold crystallization at temperatures (T_{CC}) between -70°C to –100 °C, with the extent and rate of crystallization a function of temperature ramp rates, number of chemical and physical topological constraints, and filler content.[4-11] Yim ans St. Pierre, for example, have studied the effect of the temperature of cold crystallization in linear PDMS with the addition of silica filler.[7] Further, Cohen-Addad has studied the partial crystallization of adsorbed chains in Silica-PDMS composites and Aranguren and Andrianov, et al have noted the effects of some types of silica fillers on the heat of fusion of the crystallization event in filled PDMS.[5,6,8,10,11] In general, these studies have suggested that the addition of the silica filler provides a nucleation site for crystallization, thereby accelerating the crystallization process. In addition, the addition of the silica filler adds functional topological constraints which reduces the amount of crystallinity that ultimately develops.[6,8] None of these reports detailed the complex effect of silica-polymer interactions on a cross-linked, filled, copolymer system like those that dominate Engineering silicone products. In addition, the conclusions these reports present on the effect of silica-polymer interactions on the crystallization behaviour are drawn on the comparison of filled versus unfilled systems. There is a fundamental need to investigate the effect of surface interactions on the crystallization processes in materials where a more direct control of the surface interactions is possible without complete removal of the filler. Such subtle changes in filler-polymer interactions can be key in understanding long term performance of materials in engineering applications for prevention and stabilization efforts in material design issues.

In previous work, we detailed the effects of gamma radiation on crosslink density in a engineering filled siloxane based composite material (a silica filled, random block copolymer of 94.6 mol. % PDMS, 5.1 mol. % PDPS, and 0.3 mol. % PMVS) by solvent swelling, DMA, and NMR.[12, 13] These studies showed that hydrogen bonding at the polymer-filler interface dominates the overall apparent crosslink density of the material. Further, it was observed that samples irradiated in air suffered from a disruption of the filler-polymer interaction, while samples irradiated in vacuum did not. As noted above, it has been shown that filler-polymer interactions can be important contributors to the crystallization of polymer composites.[10,11] Such subtle changes in filler-polymer interactions can be key in understanding long term performance of materials in engineering applications for prevention and stabilization efforts in material design issues. A detailed examination of the crystallization behaviour in the system studied here was undertaken to gain additional insight into the degradation pathways and their effect on engineering and chemical properties of the polymer composite.

EXPERIMENTAL:

Materials

The random block copolymer examined in this study consisted of dimethyl (DMS), diphenyl (DPS), and methyl vinyl (MVS) siloxane monomer units. The percentages of each monomer unit in the base rubber were 94.6 mol% DMS, 5.1 mol% DPS, and 0.3 mol% MVS (NuSil Corp., Carpenteria, CA). The polymer was compounded with silica by milling with a mixture of 21.6 wt. % fumed silica (Cab-o-Sil M7D, Cabot Corporation, Tuscola, Il), 4.0 wt. % precipitated silica (Hi-Sil 233, PPG Industries Inc., Pittsburgh, Pa), and 6.8 wt. % ethoxy-endblocked siloxane processing aid (Y1587, Union Carbide Corp, Danbury, CT). Mass Spectrometry has shown the processing aid to be characterized by a broad range of molecular

weights due to a distribution of chain lengths [data not shown]. Prior to blending with the gum stock, the filler is mixed with the processing aid and heated to heating to 120 °C for 4 hr. Porous samples were formed by milling the reinforced gum with 50 volume percent of 25-40 mesh prilled urea spheres (Coastal Chem. Inc. Cheyenne, Wyoming), which were sub-subsequently washed out with water after crosslinking of the polymer. After aging at 3 weeks at room temperature, both the unfilled and silica-filled polymer gums were crosslinked with the application of heat to activate the peroxide curing agent included in the base gum. Solvent swelling experiment methods, described in detail elsewhere, quantified the molecular weight between crosslinks in the polymer network of ~24 kDa. The contribution due to the incorporation of the silica fillers reduced the effective total molecular weight between crosslinks to ~11 kDa.[12]

Samples were irradiated for various periods of time in a stainless steel container (volume ~ 2 *l*) exposed to a ^{60}Co gamma source (E_{avg}~1.2 MeV, 5 kGray/hr). Vacuum samples were encapsulated in evacuated glass tubes (pressure ~$1x10^{-4}$ torr), while air-irradiated samples were left exposed to the air environment inside the container. All experiments were performed at the same dose rate.

Characterization

DMA testing was performed (Rheometrics RMS-800 Dynamic Mechanical Spectrometer, Piscataway, NJ) in parallel plate geometry with a static compression force of 400g. Specimens were disks 1 mm in thickness and 13 mm in diameter. The sample was sheared at a frequency of *f*=6.3 rad/sec and using a ramp sequence of 20 °C from –150 °C to 20 °C at a rate of 2 ºC/min. The maximum strain placed upon the sample was 0.5%. Isothermal DMA runs were performed by cooling the sample down to -85 °C and dwelling at this temperature for times ranging from 2 to 10 hours.

DSC analyses were performed (TA Instruments, MDSC 2920, New Castle, DE) by cooling the sample at a rate of 6 °C/min. to –150 °C from room temperature. Heating of the samples was then performed at 3 °C/min. with a modulation frequency of ~0.04 °C/50 sec. Some DSC samples were analyzed with the addition of an isothermal dwell of up to 2 hours at –85 °C on the cool down cycle prior to commencing the rest of the run.

^{29}Si {^{1}H} Magic angle spinning (MAS) and Cross-polarization magic angle spinning (CPMAS) experiments were performed on a 7.05T Chemagnetics CMX spectrometer using a 7.5 mm Chemagnetics CPMAS probe. Spinning rates were 4 kHz and contact times were set at 12 ms. The Hartmann-Hanh matching condition was optimized on a powdered sample of Kaolinite. Chemical shifts were referenced to the ^{29}Si resonance of TMS.

X-ray diffraction (XRD) experiments were performed on a Siemens D500 diffractometer at room temperature and after soaking for 2 hours at –85 °C. Experiments were conducted on PDMS/PDPS cellular silicone material and on solid PDMS/PDPS model material containing no fillers or processing aid. The percent crystallinity was estimated by dividing the sum of the net crystalline peak counts by the total net intensity in the region from $5° \leq 2\theta \leq 40°$, the region where changes in the peaks occurred due to crystallization. Kinetics of the crystallization were measured by performing 15 min. scans every 30 min. at –85 °C on the material.

RESULTS AND DISCUSSION:

Results of DSC analyses shown in Figure 1 show that cold crystallization took place in the unirradiated, filled copolymers at –75 to –80 ºC (Figure 1A), did not occur in the unfilled, unirradiated copolymer (Figure 1B), at approximately -100 ºC in linear PDMS with a M_w = 150 kDa, (Figure 1C). The glass transition temperature (T_G) was observed to occur at –120 ºC while melting (T_M) was detected by an endothermic peak at –60 ºC (ΔH_M~ 2.5 J/g). Crystallization was

determined by the presence of an exothermic peak at –80 °C with a heat of cold crystallization (ΔH_C) of ~1.5 J/g. Cryogenic X-ray diffraction results have shown that the amount of crystallization in the filled copolymer was approximately 16 ± 2% of the polymer monomers [data not shown], versus the 80% in a linear PDMS sample with M_n = 150 kDa. The XRD and DSC data indicate that, as expected, the phenyl side groups, the random nature of the copolymer network, and the chemical and physical motional constraints from the crosslink sites and the filler act as effective barriers to extensive crystallization. Reduced values of the amount of crystallization have also been observed in other crosslinked and filled formulations.[5,6,8]

There are two possible components that can crystallize in the filled polymer composite: the dimethyldiphenyl copolymer and the ethoxy-endblocked short chain siloxane processing aid. The DSC thermogram of the ethoxy-endblocked siloxane processing aid shown in Figure 1D exhibited a broad crystallization at –95 ºC and melting at –70 ºC, significantly different than the copolymer system. From an engineering aspect, the role of the ethoxy-endblocked siloxane processing aid is to increase workability during mixing of the filler and polymer and to prevent the final composite from being too hard.

It is expected that the processing aid chemically bonds to the silica filler surfaces. This has been verified by ^{29}Si cross-polarization NMR analysis, as shown in Figure 2. The ^{29}Si CPMAS spectrum of a sample made from mixing 24 wt% processing aid with the cab-o-sil filler and heating to 120 °C for 4 hr is characterized by a broad resonance centered at – 19 ppm and a small narrow peak at –10 ppm. The broad resonance is asymmetric and likely reflects the broad distribution of chain lengths bonded to the surface. These peaks have been assigned to motional constrained PDMS resonances and to mobile dimethyl-ethoxy-siloxane chain ends. The later species resulted from incomplete reaction of the ethoxy end groups with the silanol sites on the silica surface. As can be seen in Figure 2, in the PDMS/PDPS filled copolymer, no resonance

assignable to unreacted chain ends was observed in the CPMAS spectrum. The copolymer spectrum consists of a sharp resonance at –22 ppm overlying a broad resonance at –18 ppm. The sharp resonance has been assigned to mobile PDMS species in the bulk polymer while the broad component has been assigned to the surface associated PDMS chains of both the polymer network and the processing aid. The ^{29}Si CPMAS data show that in the final copolymer material, no free processing aid is present and the contribution of such a species to the polymer crystallization effects would be expected to be minimal.

It would be expected that any crystallization phenomena of the processing aid would dramatically change upon surface bonding. The DSC thermogram of the same silica with chemically bonded processing aid used for the ^{29}Si NMR is shown in Figure 1E and did not exhibit any sign of crystallization, melting, or glass transition. The sample of the filled composite used to obtain the thermogram in Figure 1A had approximately one quarter of the bonded processing aid as the sample used in obtaining the thermogram in Figure 1E. Thus, the contribution of the chemically bonded processing aid on the crystallization of the filled PDMS/PDPS polymer samples was minimal and the crystallization in the composite material must be originating in the polymer network.

The crystallization of the filled polymer composite has a strong effect on the mechanical properties of the material, as expected. This is shown in a plot of storage modulus as a function of temperature shown in Figure 3. Polymer crystallization at –85 ºC causes an increase in G', G", and tan(δ) as the crystallites act as additional topological constraints and reduce the segmental mobility of the polymer chains.[14] The dramatic change in modulus caused by crystallization has been used to examine the kinetics of polymer crystallization by isothermal DMA studies. These experiments involved rapidly cooling fully dense samples to -85 ºC and tracking complex

modulus, G*, as a function of time. As crystallization occurs, the polymer composite slowly stiffens and a steady increase in G* can be observed.

Isothermal DMA results for the filled and unfilled material in both the uncrosslinked and crosslinked state are shown in Figure 4. The data shown for the filled system demonstrate that crystallization took place over a 1.8-hour period as measured by the slow increase in complex modulus during this time period. Crystallization began after a 30-minute induction period, presumably due to a nucleation effect. Without the filler present, complete crystallization took 2.2 hours for the crosslinked polymer and 2.6 hours for the uncrosslinked polymer. The increased crystallization rate in the filled polymer has been observed in other systems and was likely due to the silica filler surfaces acting as heterogeneous nucleation sites.[5]

In light of the isothermal DMA result, the DSC analysis of the composites were revisited with the addition of a 2 hour isothermal dwell at –85 ºC during the cooling cycle, in order to allow crystallization to occur to its maximum extent. The DSC analysis with the soak at –85 ºC are shown in Figure 5 for both the unirradiated and the air irradiated samples. With the addition of the 2 hour soak, a second melting peak at –75 ºC was revealed in the DSC thermogram and the amount of melting at –60 ºC increased for the unirradiated sample. For the irradiated samples, the amount of crystallization, as measured by ΔH_f appeared to decrease with increasing dose. Further, the cold crystallization event is no longer evident in these samples as adequate time has been given to crystallize the polymer during the cool down cycle. Dual melting peaks have been observed in numerous polymer systems and are proposed to be the result of partial crystallization that occurs during both the cooling and heating cycles due to ramp rate effects, of distributions of molecular weights, or the presence of isolated domains with differing crystallization behaviour.[14] It is unknown at this time if any of these particular mechanisms is responsible for the dual melting observed for these materials.

In an effort to quantify the dependence of the crystallization kinetics on the polymer crosslink density and filler-polymer interactions, we performed isothermal DMA studies on the materials that were irradiated in either air or vacuum. A plot of the changes in G* as a function of soak time at –85 ºC for the irradiated porous samples are shown in Figure 6. In general, the onset of crystallization was strongly dependent on dose. For an unirradiated sample, approximately 1.8 hours were required for full crystallization, while a sample dosed to 250 kGray took 10 hours to crystallize to the same extent. The differences between initial and final moduli for all samples were similar. These results suggest that the ultimate amount of crystallization did not change with exposure to radiation over changes in crosslink density of a factor of two; rather, it occurred to the same extent only with a longer onset time.

The kinetics of shear modulus increase due to isothermal crystallization are identical in form to overall crystallization measured by more direct techniques. The crystallization kinetic behavior is commonly described using the Avrami relationship[15] and a similar form was applied to the shear storage modulus data. To account for the increase in complex modulus from an initial to final value, the Avrami relationship was used:

$$\mathrm{Ln}[(G^*_f - G^*(t))/(G^*_f - G^*_i)] = -at^b \qquad (1)$$

where G^*_i is the initial modulus, G^*_f the final modulus and a and b are constants. The values of these parameters obtained from a fit of (1) to the data for filled, porous PDMS/PDPS copolymers exposed to different γ-radiation levels are summarized in Table 1. They show that the initial and final complex moduli as well as the exponent b are relatively constant for all levels of exposure, with the exception of the values of the exponent b for the samples irradiated in vacuum.

The most significant effect of radiation exposure observed was on the onset time to shear modulus increase. The changes in the rate once crystallization occurred were smaller than the changes observed in the onset time: the rate of crystallization after onset was roughly constant

with the exception of the 250 kGray in air sample and the samples irradiated in vacuum, as can be seen in Figure 6. A common way of indicating rate for kinetic processes that exhibit Avrami growth behavior is the inverse of the time to reach half the maximum value. From (1), this time is given by

$$t_{1/2} = \left[\frac{ln2}{a}\right]^{1/b} \tag{2}$$

The rate to half crystallization for all samples is plotted as a function of atmosphere in Figure 7. For samples irradiated in air and vacuum, exposure resulted in an increase in the time to crystallization with the samples irradiated in vacuum slower for a given cumulative dose.

It should be noted that these rates are for the increase in modulus with time due to crystallization and there is no reason to expect that modulus depends linearly on volume fraction of the crystalline phase. Crystallization likely occurs by the nucleation and growth of small and relatively rigid crystallite domains in a continuous phase of relatively soft amorphous material (above T_g). For this morphology, mechanical models for the "composite" modulus would predict a very nonlinear relation between modulus and crystalline phase volume fraction with very little increase in modulus occurring until a significant fraction of the material has crystallized[16]. If this is the case, then the growth rates calculated from shear modulus measurements will be different from the actual crystallization rates, with the main difference being an increased time to onset of crystallization measured from the shear modulus.

With this in mind, the half-time to crystallization is plotted as a function of MW (as determined from solvent swelling in toluene[12]) in Figure 8. The the rates shown in Figure 8 do appear to be dependent on changes in molecular weight between crosslinks (MW) and the strength of the bonding between the filler and the polymer. For the samples irradiated in vacuum,

a simple empirical trend between MW and time to crystallization was observed. For samples irradiated in air, however, no such trend was observed.

We have previously reported the detailed dependence of the cumulative dose and the changes in molecular weight in these materials.[12,13] In general, increased exposure caused decreased crosslink density through radiative crosslinking. Increases in crosslink density decrease the chain mobility and increase the time and energy required to reorder. In air, it was observed that the crosslinking in the polymer network was accompanied by an initial disruption in the filler-polymer interaction, while in vacuum atmospheres, it was observed that crosslinking in the polymer network was accompanied by an increase in the polymer-filler interaction. It has already been mentioned that it is likely polymer chains adsorbed or otherwise interacting with the silica filler act as a nucleation site and catalyze crystallization rates. As a result, in samples irradiated in air to low cumulative doses (< 50 kGray) provide fewer nucleation sites and the crystallization would be expected to slow. Increased interactions between the filler and the polymer might also slow the crystallization by decreasing the motional properties of the adsorbed chains. As a result, for the samples irradiated in vacuum might be expected to be characterized by an empirical trend as observed here. The changes occurring in samples irradiated in air, however, might be expected to initially follow a reverse trend before increasing again at higher doses – as illustrated by the dashed line shown in Figure 8.

It is unknown at this time exactly where additional crosslinking during irradiation occurs along the siloxane polymer backbone. If crosslinking occurs across dimethyl groups, then the extent of crystallinity should decrease with dose. On the other hand, if irradiation-induced crosslinking occurs across the diphenyl groups, then the extent of crystallinity may not necessarily be affected. Given that the ultimate extent of crystallinity is unchanged upon

irradiation, it is likely that the crystallization is occurring in the diphenyl regions of the PDMS/PDPS base copolymer.

CONCLUSIONS:

DSC and DMA techniques were used to show that silica filled and unfilled PDMS/PDPS composites exhibit cold crystallization at –85 ºC. Isothermal DMA analysis shows that crystallization takes place over a period of 1.8 hours; the time to reach the maximum extent of crystallinity increases with γ-irradiation due to changes in the filler-polymer interaction. However, the ultimate amount of crystallization does not decrease with increasing radiation dose although the molecular weight between crosslinks has been shown to decrease with dose. It is postulated that this is due to the crosslinking occurring in the non-crystallizing, phenyl-containing regions of the polymer. Unfilled copolymer systems are shown to take longer for crystallization to be initiated, presumably due to a lack of the heterogeneous nucleation sites provided by the filler surfaces.

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FIGURE CAPTIONS

Figure 1. DSC thermogram of (A) the silica filled PDMS/PDPS copolymer; (B) the unfilled PDMS/PDPS copolymer; (C) the linear PDMS model material; (D) the processing aid; and (E) the processing aid chemically bonded to the silica filler. No soak time was applied for these experiments. Data has been shifted vertically for visual clarity.

Figure 2. ^{29}Si CPMAS spectrum of (A) the processing aid and silica filler after reaction at 120 °C for 24 hrs, and (B) the filled, copolymer composite. Additional resonances were observed at ~-100 ppm due to the silica filler silanol sites and are not shown.

Figure 3. Plot of G', G", and tan(δ) as a function of temperature from variable temperature DMA for the high PDPS filled copolymer. G" and tan(δ) have been multiplied by four to ease comparison to G'.

Figure 4. Change in G* as a function of soak time at –85 °C for the filled, unfilled, and unfilled, uncrosslinked copolymer. (A) Raw data and (B) Normalized data.

Figure 5. DSC thermograms of irradiated copolymers with a 2 hr soak time at –85 °C. Data has been shifted vertically for clarity.

Figure 6. Change in G* as a function of soak time at –85 °C for the filled porous copolymer (A) irradiated for the indicated doses in air and (B) irradiated in vacuum.

Figure 7. Plot of half time to crystallization as a function of cumulative dose for samples irradiated in air (filled diamonds) and vacuum (unfilled diamonds)

Figure 8. Plot of half time to crystallization as a function of molecular weight between crosslinks for filled copolymers irradiated in air (filled diamonds) and vacuum (unfilled diamonds). Curves are guides to the eye.

TABLES.

TABLE 1. Avrami parameters for kinetics of shear modulus increase at –85 °C.

Exposure (kGray)	Molecular Weight (g/mol)	$\ln G_i^*$ (Pa)	$\ln G_f^*$ (Pa)	b	a
Pristine	24547	12.982	14.74	5.15	0.900
5 in Air	23277	13.064	14.817	4.83	0.876
10 in Air	32000	13.007	14.774	4.93	0.342
30 in Air	34700	12.988	14.685	5.18	0.113
50 in Air	26149	12.970	14.670	5.12	0.132
100 in Air	26377	13.107	14.778	5.00	0.0124
250 in Air	21400	13.135	14.727	4.19	6.32×10^{-4}
50 in Vac.	21507	13.063	14.830	3.51	0.500
30 in Vac.	19078	13.070	14.800	3.56	9.15×10^{-2}
80 in Vac.	13357	13.171	14.798	3.87	4.21×10^{-3}

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Figure 1.

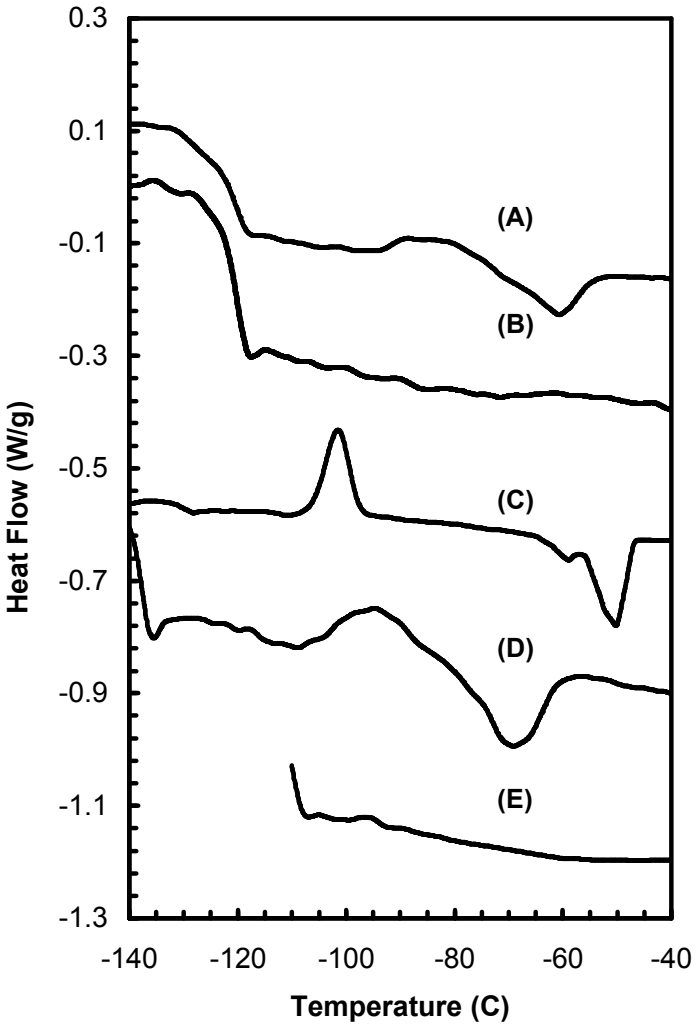

0.3
0.1
-0.1
-0.3
-0.5
-0.7
-0.9
-1.1
-1.3
Heat Flow (W/g)
-140
-120
-100
-80
-60
-40
Temperature (C)
(A)
(B)
(C)
(D)
(E)

Figure 2.

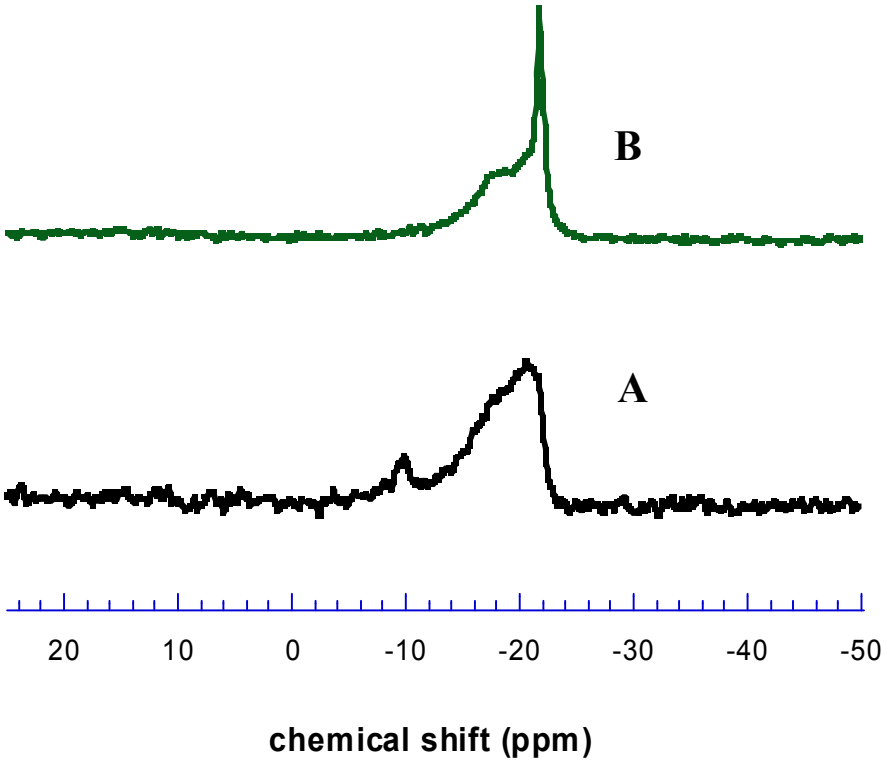


Figure 3.

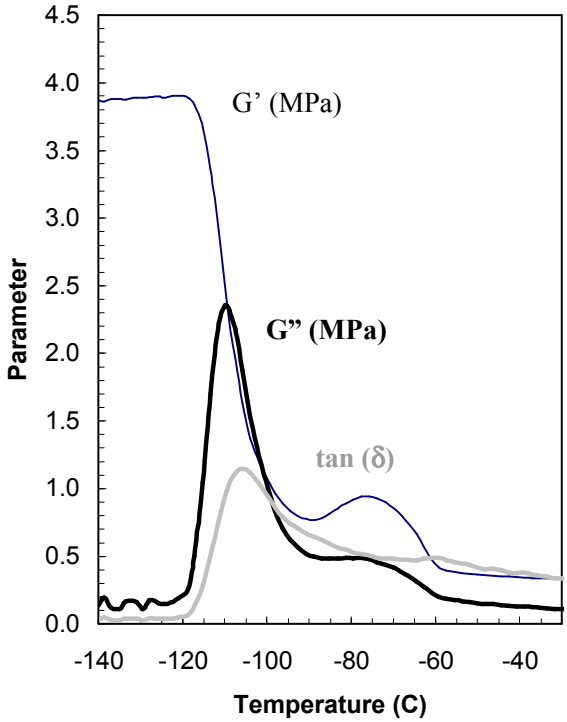
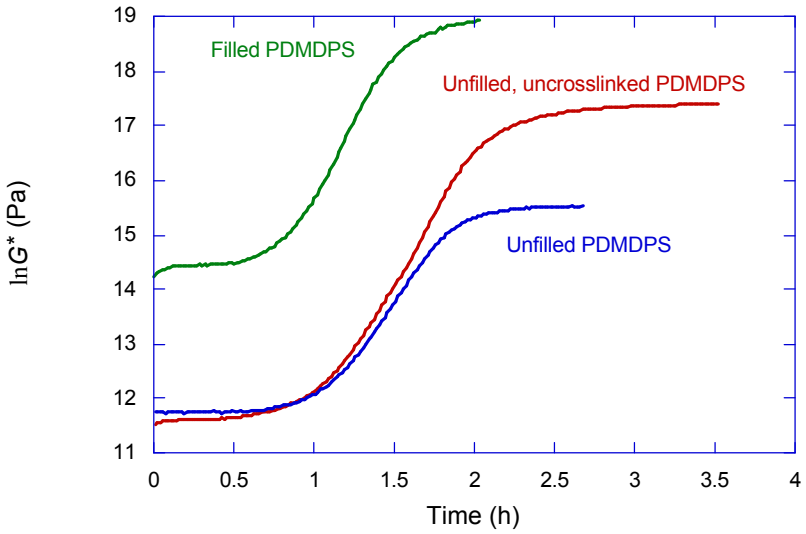

4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
Parameter
G' (MPa)
G" (MPa)
tan (δ)
-140
-120
-100
-80
-60
-40
Temperature (C)

Figure 4.

(A)


Filled PDMDPS
Unfilled, uncrosslinked PDMDPS
Unfilled PDMDPS
lnG* (Pa)
Time (h)
19
18
17
16
15
14
13
12
11
0
0.5
1
1.5
2
2.5
3
3.5
4

(B)

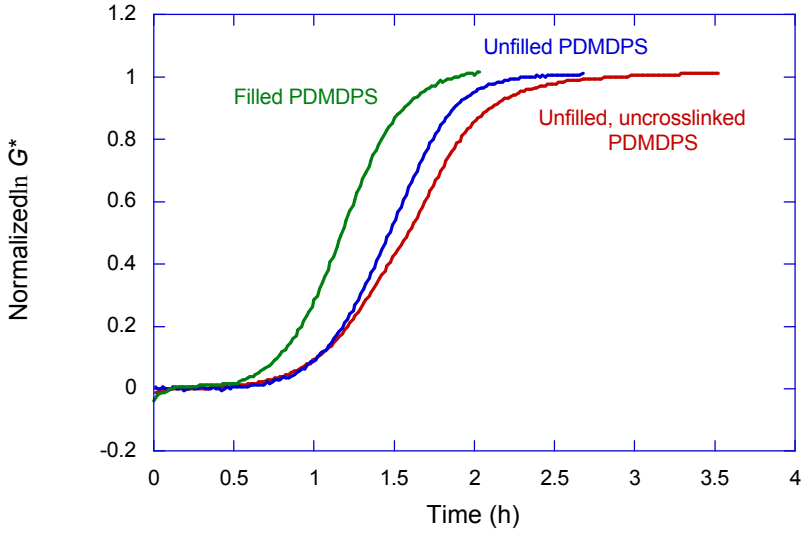

Unfilled PDMDPS
Filled PDMDPS
Unfilled, uncrosslinked PDMDPS
Normalized ln G*
Time (h)
1.2
1
0.8
0.6
0.4
0.2
0
-0.2
0
0.5
1
1.5
2
2.5
3
3.5
4

Figure 5.

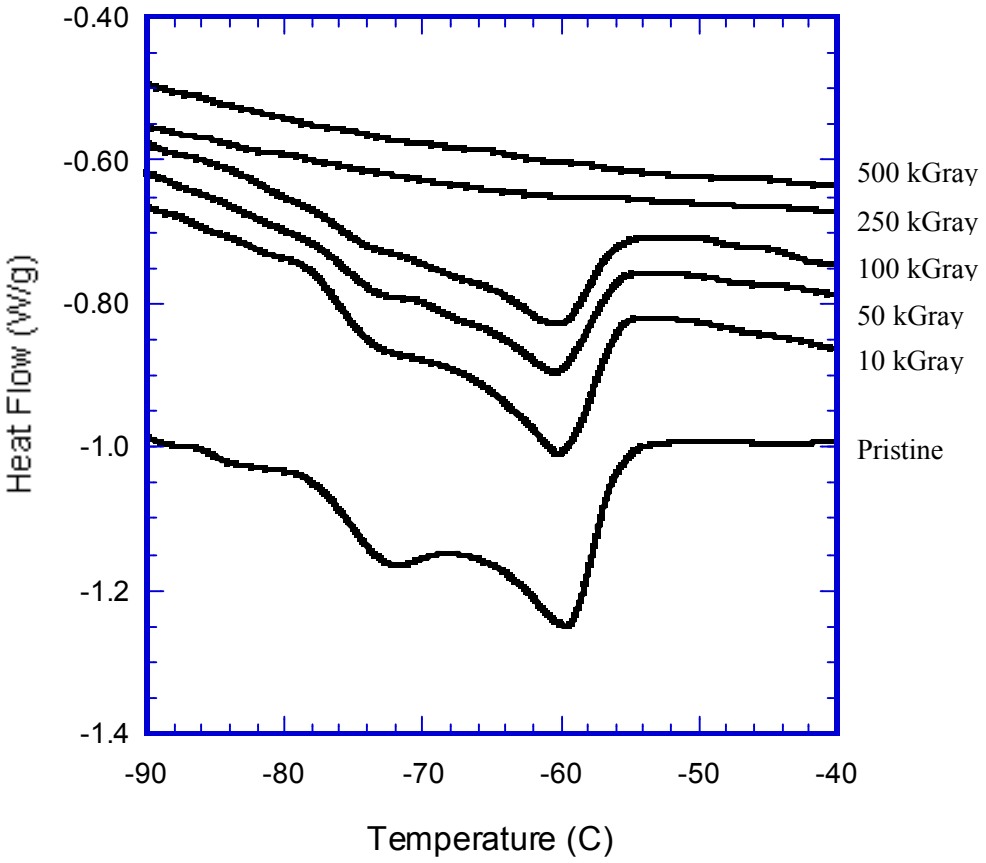
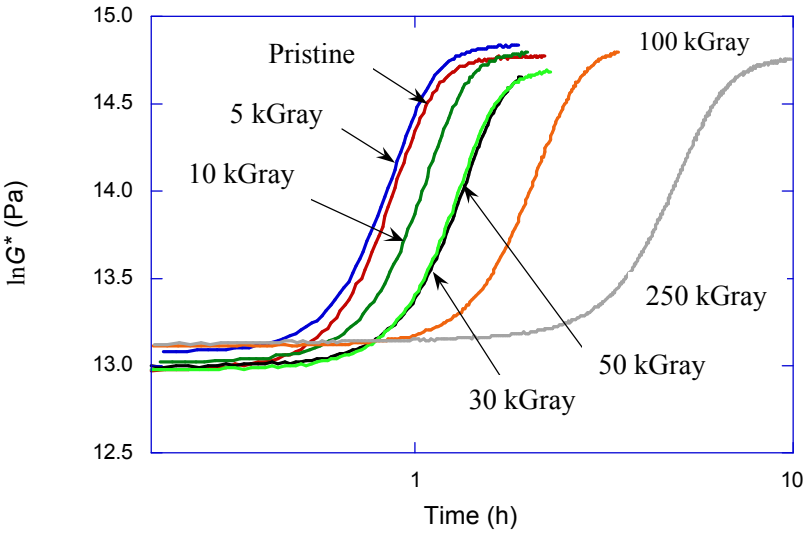

-0.40
-0.60
-0.80
-1.0
-1.2
-1.4
Heat Flow (W/g)
-90
-80
-70
-60
-50
-40
Temperature (C)
500 kGray
250 kGray
100 kGray
50 kGray
10 kGray
Pristine

Figure 6

(A)


15.0
14.5
14.0
13.5
13.0
12.5
lnG* (Pa)
1
10
Time (h)
Pristine
5 kGray
10 kGray
30 kGray
50 kGray
100 kGray
250 kGray

(B)

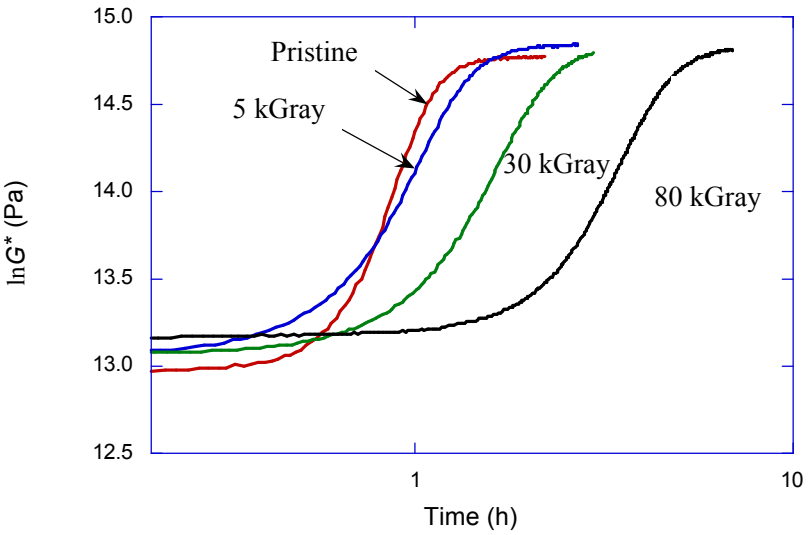

15.0
14.5
14.0
13.5
13.0
12.5
lnG* (Pa)
1
10
Time (h)
Pristine
5 kGray
30 kGray
80 kGray

Figure 7

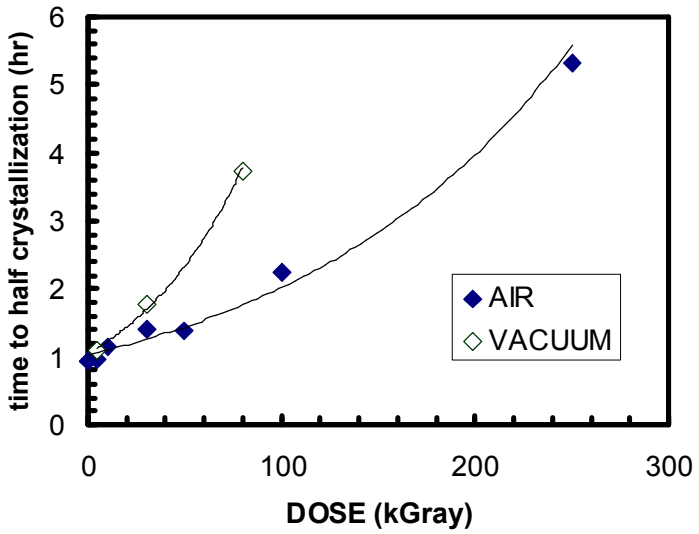

time to half crystallization (hr)
0
1
2
3
4
5
6
0
100
200
300
DOSE (kGray)
AIR
VACUUM

Figure 8.